NAIC-ID(RS)T-0496-94

NATIONAL AIR INTELLIGENCE CENTER

LUMINESCENCE PROPERTIES OF $ZnWO_4:Cr^{3+}$ LASER CRYSTALS

by

Zang Jingcun, Wu Shaohua, Ma Yue

HUMAN TRANSLATION

NAIC-ID(RS)T-0496-94 30 March 1995

MICROFICHE NR:95C000131

LUMINESCENCE PROPERTIES OF $ZnWO_4:Cr^{3+}$ LASER CRYSTALS

By: Zang Jingcun, Wu Shaohua, Ma Yue

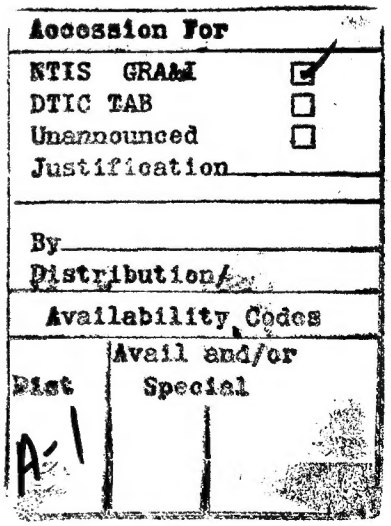
English pages: 7

Source: Zhongguo Jiguang, Vol. 18, Nr. 6, June 1991; pp. 446-449

Country of origin: China
Translated by: Leo Kanner Associates
F33657-88-D-2188
Requester: NAIC/TATD/Larry Ward

GRAPHICS DISCLAIMER

All figures, graphics, tables, equations, etc. merged into this translation were extracted from the best quality copy available.



LUMINESCENCE PROPERTIES OF $ZnWO_4:Cr^{3+}$ LASER CRYSTALS

Zang Jingcun, Wu Shaohua, and Ma Yue, of Beijing Polytechnic University, Beijing 100022

Abstract: Luminescence properties of Zn $WO_4:Cr^{3+}$ laser crystals were investigated. $^4T_2$ energy level of Cr^{3+} splitted to three levels, 13550, 14205 and 14706 cm^{-1}, and the Stokes-shift of luminescence spectra is 236 nm. The best intensity peak of emission is at 912 nm. If the excitation wavelength was selected as 608 nm and doping concentration was 0.01 wt%, a broad emission band would be observed at 532 nm excitation.

Key words: $ZnWO_4:Cr^{3+}$ crystals, luminescence, spectra

In recent years, solid tunable laser crystals have seen considerable development. Since Cr^{3+} ions are stable in electrovalence and exhibit wide absorption bands, there is wide-band fluorescence emission with $^4T_2 \rightarrow {}^4A_2$, therefore there have been considerable widespread research on various materials of Cr^{3+} as the excitation agent [1,3]. $ZnWO_4:Cr^{3+}$ laser crystals can execute continuous and tunable laser oscillation within the frequencies 900 to 1080nm, so these crystals are emphasized by researchers [4]. However, since the $ZnWO_4$ structure has low symmetry, and since there is still inconsistent views in the analysis of optical spectra, and high-grade complete monocrystals are not readily available, there has not been extensive studies on their luminescence properties. This paper reports on research results on the luminescence properties of high-grade monocrystals with dislocation density lower than $5x10^2 cm^2$. These monocrystals were grown by the authors.

I. Experimental Results and Discussion

1.1. Absorption spectra

The zinc tungstate monocrystals are of the P2/C space group. After doping with x-ray analysis, there is no change in its fundamental structure. With different amounts of the dopant Cr^{3+}, the cell parameters change slightly. When the concentration of Cr_2O_3 is 0.05% by weight (indicating the constituent concentration, as below), the crystal cell volume is at a minimum. The crystal cell parameters are a=0.46835nm, b=0.56910nm, c=0.49211nm, $\beta=90.53^0$. These quantities are used as the basis for x-ray orientation. The direction of light passage is the polarization absorption light spectrum for [100] and [010], as shown in Fig. 1. The test instrument is the UV-265 ultraviolet visible light spectrophotometer. From the figure, we can see that there are two main absorption bands for $ZnWO_4:Cr^{3+}$. The main absorption bands correspond, respectively, to $^4T_1$ and $^4T_2$ energy levels, based on splitting of $d^3(^4F)$ electrons in an octahedral field [5]:

$$^4A_2 \rightarrow {}^4T_2 = \Delta$$

$$^4A_2 \rightarrow {}^4T_1 = 7.5B + 1.5\Delta - (b^-)$$

In the equations, $b^- = \frac{1}{2}[(9B-\Delta)^2+144B^2]^{1/2}$, 于是有

then we have $\frac{E_2(^4T_1)}{E_1(^4T_2)} = \frac{1}{\Delta/B}\left\{7.5+1.5\Delta/B-\frac{1}{2}\sqrt{(9-(\Delta/B)^2+144}\right\} = f(\Delta/B)$

let $E_2 = 20032\,cm^{-1}$, $E_1 = 14124\,cm^{-1}$,

Plot a graph $f(\Delta/B)\sim\Delta/B$, and then we obtain $\Delta/B=23.5$, $B=601cm^{-1}$, and $C\approx 4B=2404cm^{-1}$. Since $ZnWO_4:Cr^{3+}$ are monoclinic crystals, octahedral Cr^{3+}-O is seriously deformed, causing a further split of the $^4T_1$ and $^4T_2$ energy levels of Cr^{3+} ions. The $^4T_1$ level splits into $205706cm^{-1}$ (487nm) and $19531cm^{-1}$ (513nm). The $^4T_2$ level splits into three levels $\varepsilon=14706cm^{-1}$, $\delta=14205cm^{-1}$, and $\eta=13549cm^{-1}$. In the polarized absorption spectrogram of E//C in Fig. 1b, there is a ^2E peak in the vicinity of 810nm. From Fig. 1, we can see that the polarization property is very clear. For instance, when the direction of light passage is [100], there

is a considerable difference in light spectra of E//C and E//b. When the direction of light passage is [010], there is also little difference between shapes of light spectra for E//C and E//a, and the absorption value is much higher than that of E//a; these facts should be considered in experiments on laser excitation.

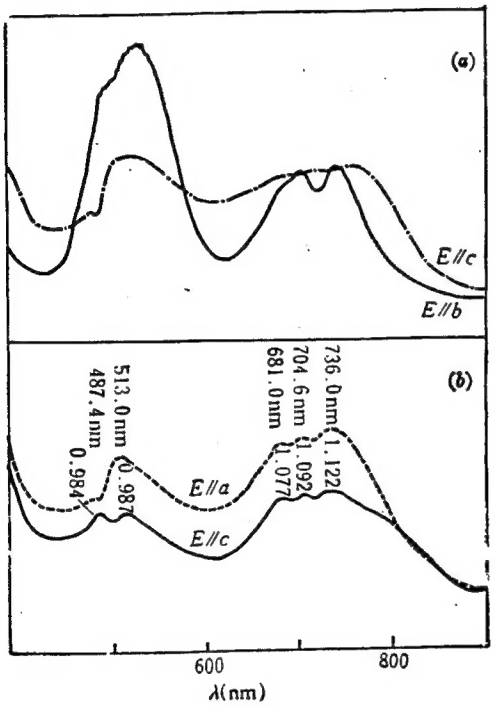


Fig. 1 Absorption spectra of $ZnWO_4:Cr^{3+}$ crystal
(a) optical direction (100);
(b) optical direction (100)

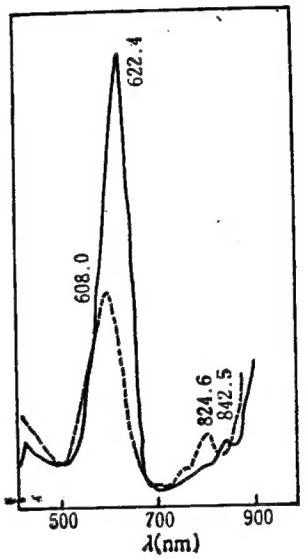


Fig. 2 Excitation spectra of $ZnWO_4:Cr^{3+}$ crystal at room temperature (λ_{em}=920 nm)
——Cr_2O_3 0.01% wt concentration
——Cr_2O_3 0.1% wt concentration

1.2. Excitation light spectra

Fig. 2 shows the light excitation spectra of $ZnWO_4:Cr^{3+}$. The excitation spectra are measured with the Daojin [Japanese name in Chinese pronunciation] RF-540 fluorescence spectrograph. If 912nm is used as the monitoring wavelength, the resulting excitation spectra is related to the Cr^{3+} dopant concentration. When the Cr^{3+} dopant concentration is greater than 0.05%, the excitation peak is at 608nm. When the concentration is less than 0.05%, the peak moves to 622.4nm. This shift is related to adjustment of the crystal lattice. As shown by x-ray analysis,

when the Cr^{3+} dopant concentration is 0.05%, the crystal cell volume is at a minimum. Therefore, when the lattice position occupied by Cr^{3+} is such that the dopant concentration is high, the Cr-O spacing changes, causing two different positions for the excitation absorption peaks. In the authors' view, this excitation absorption peak is caused by the $^2T_1$ energy level split off from the ^2G energy level.

1.3. Fluorescence spectra

Fluorescence spectra are measured with the RF-540 fluorescence spectrograph. To monitor with the instrument, a photoelectric multiplier is used, the multiplier is of the same type as that used in light measurements, such that the influence of a change in light source intensity can be eliminated. Fig. 3 is the fluorescence spectra based on the energy level position of the absorption spectra while fixing the excitation wavelength. Relative to the fluorescence peak intensity, the change is minor. It can be determined that these three energy levels are $^4T_2$ as the result of low-symmetry splitting. From Fig. 4, we can see that Stokes displacement is very close after splitting of the $^4T_2$ energy level, at 3753, 3567, and 3345cm^{-1}, respectively. These are caused by oscillation of the crystal lattice. With the red shift in wavelength, Stokes displacement also slightly increases in value.

The dopant concentration also considerably influences Cr^{3+} luminescence. Fig. 6 indicates the influence on fluorescence intensity due to the dopant concentration. When the concentration is between 0.005 and 0.01% by weight, the fluorescence is the most intense. With increase in concentration later on, the fluorescence drops exponentially. At 0.05% by weight, the luminescence intensity again begins to increase. However, after the concentration becomes greater than 0.08% by

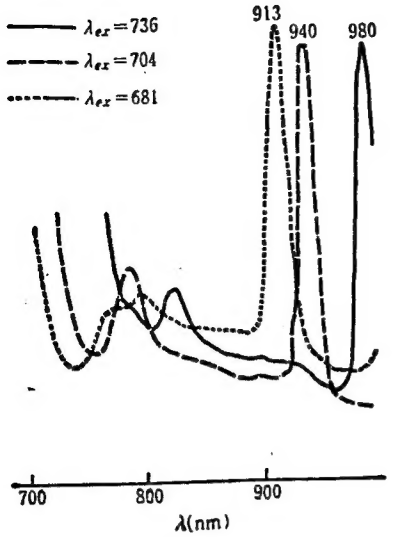


Fig. 3 Emission spectra of $ZnWO_4:Cr^{3+}$ crytsal at room temperature

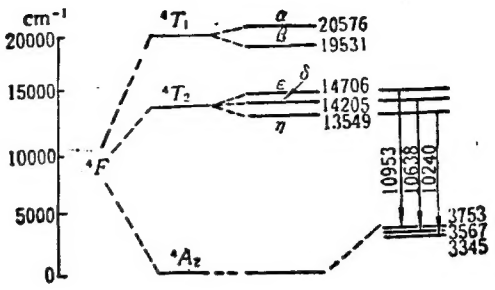


Fig. 4 Energy level diagram of Cr^{3+} in $ZnWO_4:Cr^{3+}$ crystal

weight, the luminescence intensity begins to saturate. However, in the vicinity of 0.1% weight, concentration quenching sets in, thus the luminescence intensity clearly decreases.

Fig. 6 shows the different kind of influence on luminescence with variation in excitation wavelength. The fluorescence peak is the strongest when excited with 608nm. This is possibly caused by energy shift in $^2T_1$ and $^4T_2$ energy levels. However, it is not easily available for intensive excitation source at 608nm, so excitation is at the 532nm wavelength (double frequency Nd^{3+}:YAG laser). Although the intensity drops quite drastically, the position of the wavelength peak is the same, and the bandwidths are close to each other. However, there is still sufficient intensity, therefore $ZnWO_4:Cr^{3+}$ is a very promising new kind of laser crystal.

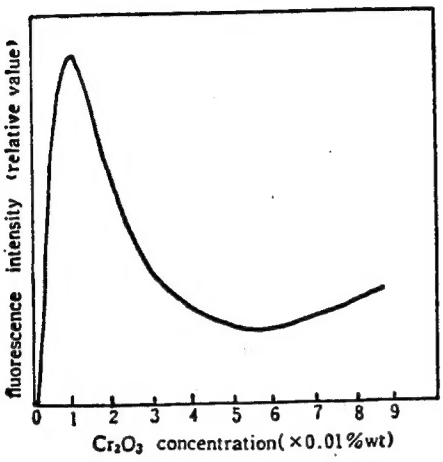


Fig. 5 Effect of Cr^{3+} ion concentration on emission intensity

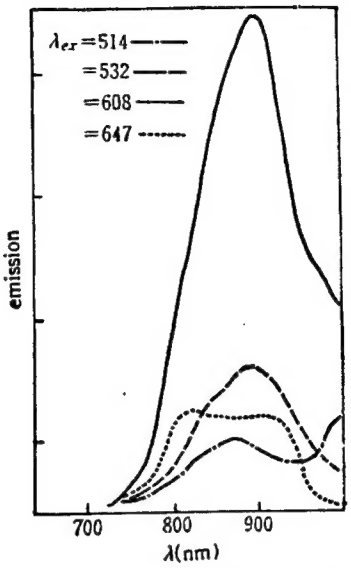


Fig. 6 Emission spectra excited by various wavelengths

Wang Liangmao took part in growing the crystals. Comrade Xu Zuyan, of the Institute of Physics of the Chinese Academy of Sciences, gave much assistance in the experiments on laser excitation. The authors express their gratitude to both of them. In addition, the authors are grateful to professor Zhang Kecong, for his concern and guidance in the investigation.

The research was funded by the State Natural Science Foundation. The paper was received for publication on 21 November 1989.

REFERENCES

1 G. Huber *et al.*, *J. Luminescence*, **39**, 259~268 (1988)
2 D. Vivien *et al. J. Luminescence*, **39**, 29~33 (1987)
3 K. Petermann *et al.*, *J. Luminescence*, **31** & **32**, 71~77 (1984)
4 W. Kolbe *et al.*, *IEEE J. Quant. Electr.*, **QE-21** (10), 1596 (1985)
5. Marfunin, A.S., Kuangwu wulixue daolun [Mineral Physics], Geology Publishing House, 1984, p. 67.

DISTRIBUTION LIST

DISTRIBUTION DIRECT TO RECIPIENT

ORGANIZATION	MICROFICHE
B085 DIA/RTS-2FI	1
C509 BALLOC509 BALLISTIC RES LAB	1
C510 R&T LABS/AVEADCOM	1
C513 ARRADCOM	1
C535 AVRADCOM/TSARCOM	1
C539 TRASANA	1
Q592 FSTC	4
Q619 MSIC REDSTONE	1
Q008 NTIC	1
Q043 AFMIC-IS	1
E051 HQ USAF/INET	1
E404 AEDC/DOF	1
E408 AFWL	1
E410 AFDIC/IN	1
E429 SD/IND	1
P005 DOE/ISA/DDI	1
P050 CIA/OCR/ADD/SD	2
1051 AFIT/LDE	1
P090 NSA/CDB	1
2206 FSL	1

Microfiche Nbr: FTD95C000131
NAIC-ID(RS)T-0496-94